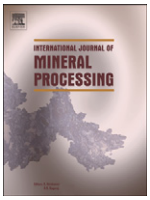
International Journal of Mineral Processing 127 (2014) 23–27

Contents lists available at ScienceDirect

International Journal of Mineral Processing

journal homepage: www.elsevier.com/locate/ijminpro



The use of dextrin in purification by flotation of molybdenite concentrates

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ARTICLE INFO

Article history:
Received 22 March 2013
Received in revised form 17 December 2013
Accepted 25 December 2013
Available online 7 January 2014

Keywords:
Molybdenite concentrates
Flotation
Dextrin
Talc

ABSTRACT

The process of flotation is commonly used for the recovery of molybdenite from mine tailings, but it produces low-content concentrates, thereby resulting in a product with low economic value. The low economic value is due to the presence of talc, which is a naturally hydrophobic mineral that is also floated with the molybdenite during the flotation process. Separability studies were conducted in a Partridge–Smith cell using dextrin as a molybdenite depressant in solution at different concentrations and pH values to produce a technical-grade concentrate (i.e., 90% MoS_2). These basic studies were accompanied by measurements of the zeta potential and contact angle, which was determined by the capillary rise method. The results of these floatability studies were used in bench tests of flotation, which were performed in a Denver D-12 cell. A molybdenite concentrate of 93.4% MoS_2 was obtained when dextrin was used at a concentration of 100 g/t.

1. Introduction

In Brazil, there are no official reserves of molybdenum, and the unofficial reserves are modest. Therefore, the molybdenum ore (molybdenite) generated as a co-product or by-product of emerald mining in the region of Campo Formoso, BA, has arisen as an economic recovery option.

More than 20,000 people are economically dependent on emerald mining in Campo Formoso and on the flotation of molybdenite in the tailings from its exploitation and processing. The lack of information about the processing of this mineral, the disposal of the tailings, the value of the minerals produced, and the legal and environmental aspects with regard to the mining is well known.

The process of flotation is used for the recovery of molybdenite from mine tailings to produce low-content concentrates, resulting in a product with low economic value. The molybdenite concentrate produced in Campo Formoso contains 83.5% MoS_2 (50% Mo), which is less than the internationally commercialised product that contains >90% MoS_2 (54% Mo). A characterisation of the molybdenite concentrate revealed low concentrations of MoS_2 and high concentrations of MgO and SiO_2, which are indicative of the presence of talc, phlogopite, chlorite, and clinochlore (Braga, 2013).

Many studies have been performed to understand the mechanisms of depression and dispersion to separate the molybdenite from insoluble and strongly hydrophobic minerals, such as talc (Vincent and Shirley, 1985).

Kelebek et al. (2001) had used adhesion tension diagrams to characterize the wettability of molybdenite and talc, in sodium lignosulphonate and methyl-isobutyl carbinol solutions, at pH 7.2. There was a linear correlation found between the adhesion tension ($\gamma_{LV}.\cos\theta$) and interfacial tension (γ_{LV}); the adsorption relative density is indicated by the slope value (β). The results showed that the adsorption relative density of lignosulphonate at the solid–liquid interface of molybdenite face was larger than the one obtained to the talc interface, by a factor 2.7. Once the floatability of both minerals molybdenite and talc is mostly controlled by the surface properties of their cleavage planes, it would be expected that molybdenite is depressed rather than talc. Considering the experimental results it is possible to suppose that hydrophobic bond is the supporting mechanism for the adsorption of sodium lignosulphonate on the molybdenite surface.

Ansari and Pawlik (2007a,b) studied the adsorption and Hallimond tube flotation of chalcopyrite and molybdenite in the presence of lignosulphonates, which are strongly anionic polyelectrolytes obtained as by-product of wood processing. The results suggested that it is possible to selectively float chalcopyrite from molybdenite, due to the selective action of lignosulphonate regarding molybdenite surface, in accordance to the results presented by Kelebek et al. (2001). The adsorption process was controlled by electrostatic forces and chemical interactions between the anionic polyelectrolyte and metal-hydroxy sites on the mineral surfaces.

Molybdenite exhibits a laminar crystalline structure that is based on two types of chemical bonds, including covalent bonds between S–Mo, whose ruptures generate high-energy sites on the surface known as edges, and van der Waals interactions between the S–Mo–S layers, whose ruptures generate low-energy sites known as faces. These distinct sites constitute a heterogeneous intrinsic surface according to

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http://dx.doi.org/10.1016/j.minpro.2013.12.007

the ratio of the faces to the edges (Castro and Correa, 1995). Strong covalent bonds exist in the interior of the layers that, when broken, generate free high surface energy, i.e., hydrophilic sites (Jara and Castro, 2006).

Recently, influenced by the study of Chander and Fuerstenau (1972), López-Valdivieso et al. (2012) performed an in-depth study of the nanoscale surface properties of molybdenite using atomic force microscopy (AFM). The effects of pH and the presence of Ca^{2+} on the floatability and the electrokinetic properties of molybdenite were investigated by evaluating the surface texture of the mineral. They concluded that the molybdenite faces are naturally heterogeneous and are composed of microcrystals of MoS_2 with nanofaces and nanoedges. The authors also found that the faces are not completely hydrophobic, possibly due to the presence of the nanoedges, which generate hydrophilic sites. These nanoedges have negative electrical charges that increase with increasing pH and prevent the interaction of the air bubbles with the surfaces (faces) of the molybdenite crystals, consequently promoting the low floatability of molybdenite.

Beaussart et al. (2012) evaluated the adsorption of three modified dextrin samples (TY, CM and HP) in molybdenite surface using AFM (atomic force microscope) imaging, contact angles measurements and floatability in Denver cell. It was noticed that the adsorption of the different dextrin samples occurred randomly on molybdenite surface, therefore the adsorbed amount is directly related to the polymer molecular weight. The three polymers reduced the floatability of molybdenite, when used a concentration of 100 $mg \cdot L^{-1}$.

Gerson et al. (2012) examined samples of concentrate and tails of Cu–Mo batch flotation via SEM (scanning electronic microscope) with EDX (X-ray fluorescence energy dispersive) analysis. The concentrate micrographs show fully liberated and clean surface molybdenite particles, while tail images show both unliberated and liberated molybdenite particles; therefore these particles are heavily oxidised and with surface associations of magnesium silicates, increasing its hydrophilic characteristic.

The purpose of this study was to evaluate the use of dextrin as a selective depressant during the separation of molybdenite and talc minerals by flotation, thus adding value to the concentrate produced in Campo Formoso.

2. Methodology

2.1. Materials and reagents

The molybdenite used in the floatability tests in the Partridge–Smith cell contained approximately 90% MoS_2. The sample was treated with dilute nitric acid (0.1 M) to eliminate oxide layers; and dilute potassium hydroxide (0.1 M) to remove any hydrophobic impurities or residual reagents. After each leaching step the residues were removed by washing the sample with distilled water. The sample was dried in a vacuum desiccator.

Macrocrystalline talc, containing 30.7% MgO, was provided by the Mineração Paranaense [Paranaense Mining] and was crushed in a porcelain mortar to a particle size of less than 150 μm.

Before initiating the tests, the molybdenite and talc samples were subjected to an ultrasound treatment for 5 min to disperse the minerals more effectively. The particle sizes of both minerals ranged from 37 to 74 μm.

The dextrin (Sigma-Aldrich, Rio de Janeiro, Brazil), which was used as the depressant reagent, had a molecular weight of approximately 8900 Da, as measured with a Zetasizer Nano ZS instrument using the static light scattering (SLC) technique. Various concentrations of dextrin solutions were prepared from a stock solution of 1000 ppm.

Methyl isobutyl carbinol (MIBC) was used as a frothing agent at a concentration of 100 ppm, and potassium hydroxide and hydrochloric acid (analytical grade) were used as pH regulators. Potassium chloride was used at a concentration of 10^{-3} moles/L to maintain ionic strength during the flotation tests.

2.2. Methods

The purpose of the floatability tests was to verify the influence of pH on the concentration of dextrin and the floatability of the molybdenite and talc minerals.

The pH of the mineral suspension, which was prepared using 3 g of the sample, was adjusted in a beaker with magnetic agitation. Next, the suspension was conditioned first with the depressant reagent for 5 min and then with the frothing agent (MIBC) for another 5 min.

Following conditioning, the suspension was floated in the 250 mL Partridge–Smith cell for 3 min. Pressurised filtered air, which was introduced into the cell with a porous plate at a flow rate of 1 L/min that was adjusted by a rotameter, was used to generate bubbles. The agitation of the mineral suspension was maintained using a magnetic bar.

The flotation tests were performed at pH values of 2, 4, 6, 8, 10, and 12, and the depressant concentration was fixed at 100 ppm. Additional tests were performed to confirm the influence of the depressant concentration on the floatability of the talc and molybdenite.

After the flotation tests, the sunken and floated products were dried and weighed to evaluate the floatability (the mass relationship between the floated product and the sum of the floated and sunken products) according to Eq. (1)

$$\text{Floatability}(\%) = 100 \cdot \frac{\text{floated mass}}{\text{floated mass} + \text{sunken mass}}. \tag{1}$$

All of the flotation tests were performed in triplicate, and the results that exhibited deviations greater than 5% were repeated.

Measurements of the potential were performed using a Zetasizer Nano-ZS instrument in the presence and absence of depressing agents to verify the influence of pH on the zeta potentials of the molybdenite and talc. This instrument possesses a coupled automatic titrator that allows for the determination of the zeta potential over a broad pH range without the need to exchange samples (Malvern, 2009).

Measurements of the contact angle were performed using the capillary rise method for pure molybdenite and molybdenite conditioned with dextrin at different concentrations. The contact angle measurements by capillary rise were conducted using a Krüss K100 tensiometer. The molybdenite samples were weighed and compacted in a cylindrical tube to a height of approximately 20 mm. The tensiometer tube was 50 mm high and 10 mm in internal diameter and had a porous filter on the end that allowed for the percolation of the liquids and the retention of the compacted minerals. The measurements were performed using a non-polar solvent (*n*-hexane) and a polar solvent (water) (Viegas and Monte, 2012).

Using the modified Washburn Equation (m^2 as a function of t) (Eq. (2)), it is possible to determine the contact angle (θ) by the capillary rise method through physical measurements using the mass increase of the absorbed liquid (m) as a function of time (t) (Martins, 2009; Siebold et al., 1997).

$$\frac{m^2}{t} = \frac{c\rho^2\gamma_{LG}\cos\theta}{\eta} \tag{2}$$

where m is the mass of the liquid absorbed, t is the absorption time, ρ is the specific weight of the liquid, γ is the surface tension of the liquid, η is the viscosity of the liquid, θ is the advancing contact angle, and c is a constant.

The constant (c) is determined according to Eq. (3).

$$c = \frac{1}{2}\pi^2 r^5 n^2 \tag{3}$$